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Polar Domains in Lead Titanate Films under Tensile Strain

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Thin films of PbTiO_3 , a classical ferroelectric, have been grown under tensile strain on single-crystal substrates of DyScO_3 . The films, of only 5 nm thickness, grow fully coherent with the substrate, as evidenced by synchrotron x-ray diffraction. A mapping of the reciprocal space reveals intensity modulations (satellites) due to regularly spaced polar domains in which the polarization appears rotated away from the substrate normal, characterizing a low-symmetry phase not observed in the bulk material. This could have important practical implications since these phases are known to be responsible for ultrahigh piezoelectric responses in complex systems.

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Ferroelectrics are dielectric materials with a permanent switchable polarization. Theoretical and experimental research of ferroelectric thin films is recently attracting a lot of attention not only because of their promising technological applications in novel geometries but also because of the new fundamental understanding of ferroelectricity at the nanoscale [1].

Perovskite ferroelectric thin films are strongly affected by epitaxial strain. Clamping between the film and the substrate onto which it is deposited is known to induce shifts in critical temperatures, increase tetragonality and polarization, and change the order of the phase transition [2–7]. Some theoretical works have also predicted other interesting possibilities, such as changing the polar symmetry [7–9], engineering the domain configuration [10,11] and, for unscreened surface charges, inducing polar rotations across the thickness of the films [12].

The most interesting predictions of the stability diagrams for epitaxial tetragonal perovskite ferroelectrics tend to be those for tensile in-plane strain [7–11], as compressive strains simply induce an enhancement of tetragonal out-of-plane polarization. However, experimental verification of such predictions is difficult. This is partly because most available perovskite single-crystal substrates (SrTiO_3 , LaAlO_3 , NdGaO_3) have lattice parameters that are either very close to, or smaller than, those of typical perovskite ferroelectrics such as PbTiO_3 or BaTiO_3 . At the other end of the spectrum, substrates with bigger lattice parameters, such as perovskite KTaO_3 , have so large a mismatch that the strain is rapidly relaxed through dislocations or twin formation [13,14]. Fortunately, the recent development of new perovskite single crystals from the family of the scandates [3,4,15] bridges the gap, thereby widening the scope for strain tailoring of the films and allowing us to explore experimentally some of the above-mentioned theoretical predictions.

We have grown fully coherent thin films of the archetypal perovskite ferroelectric PbTiO_3 (PTO) under biaxial tensile strain and analyzed the reciprocal space using syn-

chrotron x-ray diffraction. The results show that polarization rotation is induced in these films. This new polar state of PTO is consistent with the so-called *ac* phase, polarization tilted in the (010) plane, and *r* phase, polarization tilted in the (110) plane. Neither symmetry exists in the parent bulk compound [16]. These findings could have important technological implications since similar low-symmetry phases, very rare in ferroelectrics, are believed to be responsible for the unusually large responses observed in the ultrahigh piezoelectrics, such as $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ and related systems [17,18]. The results thus confirm experimentally that new polar states that do not exist in bulk can be made accessible in epitaxial films through careful tuning of strain, thickness, and electrode [7,8].

Experimental studies of ferroelectricity often require either the use of electrodes, which themselves introduce important changes in the thin films [12,19], or optical methods, difficult with ultrathin films. However, in a series of seminal papers, Streiffer and co-workers have shown that polar stripe domains can be detected as satellite peaks in x-ray diffraction patterns, and that this technique can be used to measure the domains size and polar orientation [20,21] even in films as thin as 3 perovskite unit cells [21]. This technique is therefore ideally suited for the study of polar symmetry in very thin films where very few others (see Ref. [22]) can be implemented.

In this study we have deposited 5 nm thin films of PTO, using RHEED-assisted pulsed laser deposition, at 570° C and with an oxygen background pressure of 0.13 mbar (further details of the growth will be published elsewhere [23]). The films were grown either directly on [110]- DyScO_3 (DSO) crystals, or on [110] DSO with a 5 nm buffer layer of the conductive perovskite SrRuO_3 (SRO), deposited at 600° C [24]. Bulk PTO has a tetragonal structure at room temperature, with lattice parameters $a = b = 3.89 \text{ \AA}$ and $c = 4.14 \text{ \AA}$ [25]. The lattice structure of DSO is orthorhombic and [110]-oriented substrates are expected to have nearly squared in-plane lattice with

$a = 3.944\text{--}3.948$ Å and $b = 3.943\text{--}3.945$ Å at right angles [4,15], which would induce tensile strain ($a_{\text{film}}/a_{\text{substrate}} - 1$) of about 1.4% on the PTO film. The cubic structure of PTO around $T_C = 490^\circ\text{C}$, has a lattice parameter that is almost identical to the pseudocubic lattice parameter of DSO [15] and at the deposition temperature there is therefore a good lattice match between PTO and DSO, while the mismatch between SRO and DSO is only $\approx 0.4\%$ [15]; this, in combination with the reduced thickness, prevents the relaxation of either layer via misfit dislocations [26]. As it cools down below T_C , however, the drive towards the tetragonal structure introduces large in-plane strains. These may in principle be accommodated by dislocations [26], by domain twinning [10,11,13], and/or by changes in the symmetry of the films [7,8].

The synchrotron x-ray measurements were carried out in the W1 beam line at HASYLAB (DESY-Hamburg), using a 1×1 mm² monochromatic beam of 9.8 keV ($\lambda = 1.26515$ Å). Reciprocal space maps within the $H0L$ and $0KL$ zones were obtained in standard reflection geometry. Scans in the $HK0$ zone were achieved using grazing incidence diffraction (GID), in which a nonpropagating evanescent wave is used to diffract within the plane of the film. This is attained by making the x-ray beam reach the surface close to the critical angle of total reflection (0.3° in our case). The reciprocal space maps presented here have been calculated from the measured angular scans and plotted in reciprocal lattice units (r.l.u.) of the substrate (1 r.l.u. = $2\pi/3.950$ Å⁻¹, in plane, and $= 2\pi/3.942$ Å⁻¹, out of plane).

The reciprocal space maps around the (001) and (103) reflections (Fig. 1) show that the in-plane reciprocal space vectors of the film and the substrate [the sharp peaks at $L = 1$ (a) and $L = 3$ (b)] are identical (same H value in the figures), and that the films' truncation rods have the same width as the substrate peak. These observations are evidence of full in-plane coherence of the films. However, Fig. 1 also shows broad satellite peaks outside of the truncation rod. In Fig. 2 the GID reciprocal space maps within the $HK0$ plane, corresponding to the (100), (010), and (200) in-plane reflections of the film grown with a SRO buffer layer are shown, together with the scan in the

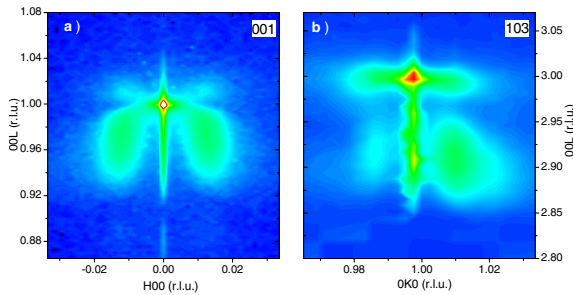


FIG. 1 (color online). Logarithmic reciprocal maps in the $H0L$ scattering plane around the 001 (a) and 103 (b) reflections for a 5 nm PbTiO₃ film directly grown on a DyScO₃ substrate. (Intensities from low to high: blue-green-yellow-red-white)

$H0L$ plane around the specular 001 reflection of the same sample. For a given sample, the satellites have the same reciprocal space separation in all reflections. This shows that they are not Bragg peaks owing to different elastic domains but originate instead from an in-plane modulation. The distance between the satellites and the Bragg peak (ΔH) yields modulation periodicities of $\Lambda = 2\pi/\Delta Q = 0.395$ nm/ $\Delta H \approx 20$ nm for the films grown with a SRO electrode, and $\Lambda \approx 30$ nm for the films grown directly on DSO.

Figure 3 shows the $HK0$ area scans around the 110 reflections of the two films. While the satellites for the film grown on a SRO electrode are oriented preferentially along the a, b pseudocubic axes (the edges of the substrate), the intensity distribution for the film grown directly on DSO is somewhat more isotropic (the same near-circular distribution with increased intensity at high H and K values was found around the 100 and 010 reflections of the same sample). We do not know the cause for this difference, although we note that both types of domain configuration have been seen before for PTO films grown on SrTiO₃ substrates [20,21].

The pseudocubic lattice parameters of the DSO substrate were found to be $a \approx b = 3.950$ Å, and $c = 3.942$ Å, while the lattice parameters of the PTO films were $a \approx b = 3.950$ Å, owing to the in-plane coherence, and $c \approx 4.07$ Å [27]. As reported by He *et al.* [5,28], the clamping to the

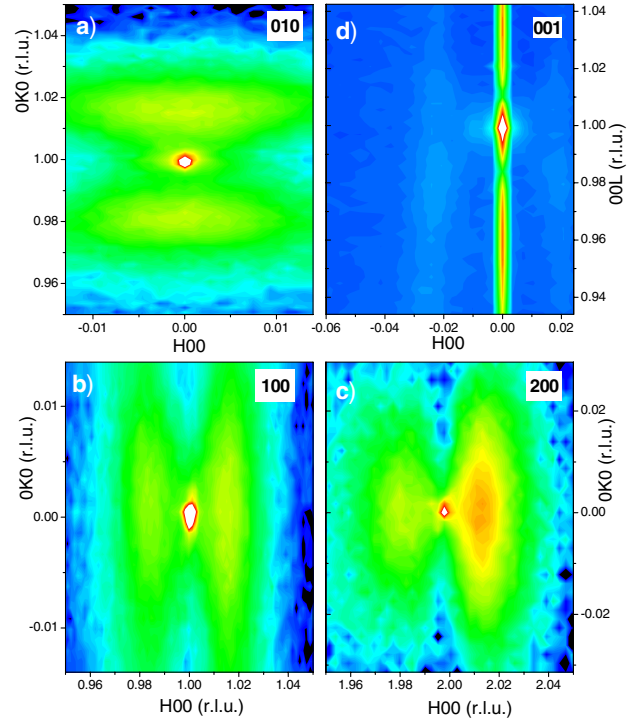


FIG. 2 (color online). Logarithmic reciprocal space maps in the $HK0$ scattering zone around the (a) 010, (b) 100, and (c) 200 reflections; and in the $H0L$ zone around the 001 reflection (d), for the film grown with a SRO electrode. [Intensities from low to high: blue (b), green (g), yellow (y), red (r), white (w)].

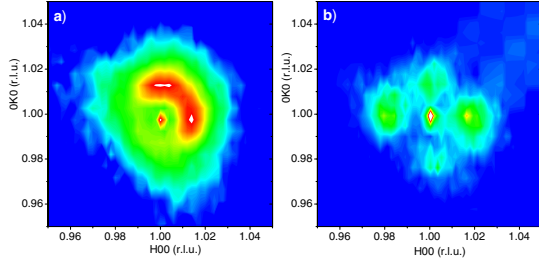


FIG. 3 (color online). Logarithmic reciprocal space maps of the $HK0$ plane around the 110 Bragg peaks of the films grown (a) directly on DSO, and (b) on DSO with a SRO bottom electrode. (Intensities from low to high: b-g-y-r-w).

substrate can decouple the symmetry of the unit cell from that of the polar shifts. Moreover, from a functional point of view, as important as the crystal structure is the polar symmetry and its domain configuration. In order to elucidate this, we turn to the analysis of the satellite peaks.

In-plane satellites in x-ray diffraction patterns may have different origins: grain boundaries, dislocations, disclinations, or other periodic structural discontinuities, or else, in ferroelectric materials, polar domains. We can disregard grain boundaries from atomic force microscope analysis of the film surface [23]. As for misfit dislocations, the good lattice match during growth makes them unlikely. In fact, the symmetry of the 100 and 010 satellites, along $[h00]$ and $[0k0]$, respectively, (Fig. 2) is inconsistent with scattering by dislocations, grain boundaries or any other periodic defects, since they should render modulation along the same directions in all reflections, which is not the case. Thus, the satellites are not due to periodic defects, but to polar domains [29]. Indeed the in-plane diffraction patterns are extremely similar to some of those observed around the 304 reflections for PTO films with vertical stripe domains in Refs. [20,21].

Stripes of alternate polarization form in a thin ferroelectric under open-circuit electrical boundary conditions in order to minimize the depolarizing field [20,30] and/or the epitaxial strain [10–12]. Since polarization is due to a shift of the Pb and Ti cations with respect to the oxygen cage, the different shift directions in the different domains produces contrast in the structure factors and causes the intensity modulations. Accordingly, there can only be structure-factor contrast (and therefore satellites) around those reciprocal lattice vectors that have at least one component parallel to the direction of the polar displacement [21]. Thus, the distribution of the satellites yields information about the domain geometry and size, and the Bragg peaks around which the satellites appear tell us about the direction of the polarization.

Therefore, from Figs. 1–3, we learn: (i) Polarization must have both in-plane and out-of-plane components, since there are satellites around $(00l)$, $(h0l)$, $(h00)$, $(0k0)$, and $(hk0)$ reflections, all with the same size, and (ii) the in-plane components of the polarization must be oriented head to head (and tail to tail) to produce modulation

parallel to the in-plane reciprocal lattice vectors. In Fig. 4 we have drawn a scheme of the domain orientations compatible with (i) and (ii). These are the ac phase ($P_x \neq 0$, $P_y = 0$, $P_z \neq 0$, monoclinic Pm) with in-plane component of the polarization along the edges of the simple cubic cell [see Fig. 4(b)], and the r phase ($P_x = P_y \neq P_z$, monoclinic space group Cm) with the in-plane component of the polarization along the face diagonals of the simple cubic cell [see Fig. 4(c)]. To reproduce the observed maps in Fig. 4(a), we consider fourfold in-plane symmetry and the existence of domain walls at 0° and 90° in both phases.

It is worth noting that the domain walls responsible for the in-plane satellites are charged, which is energetically costly. Although this is a surprising result, there are precedents of head-to-head polarized domains in other perovskites [31,32]. If the polarization initially nucleates randomly, when domains with opposite polarization grow and encounter, whether or not they switch in order to match will depend on the balance between the energy needed for the switching and the amount of charge in the wall. If this charge is neutralized by defects, or directly short circuited by the electrode, the domains will remain head to head. This picture is consistent with the bigger size of the domains in the films grown without the SRO electrode. It is

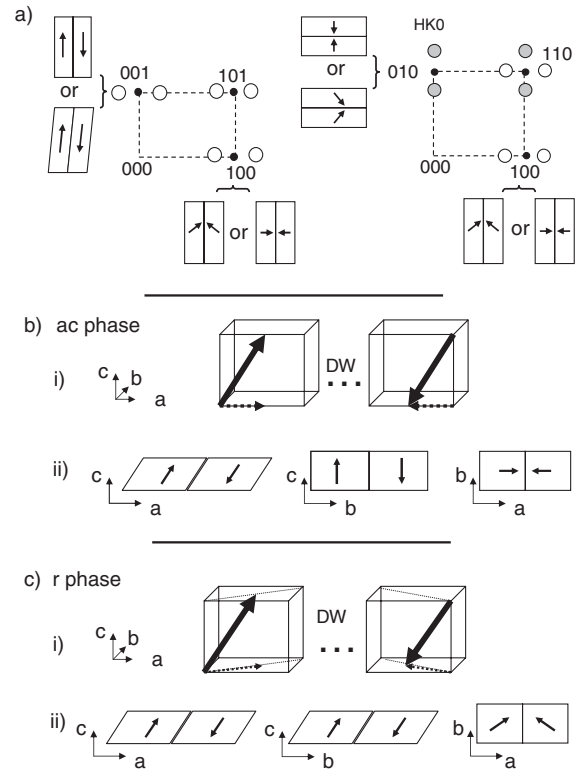


FIG. 4. (a) Schematic representation of the observed reciprocal space maps and their implication for the polar domain orientation; Polar symmetry for (b) ac phase, and (c) the r phase. In (b) and (c): (i) shows the sketch of the polar shifts in two unit cells at both sides of the domain wall and (ii) represents the projections of the polarization in the $\{100\}$ pseudocubic planes for the proposed phases and domain configurations.

also worth noting that for ultrathin films subjected to partially screened electric fields, the polar orientation has been predicted to rotate between the bottom and the top surface in such a way that in-plane head-to-head and tail-to-tail polar states appear at the top and the bottom layers of the film [12].

The out-of-plane lattice parameters are the same for the films grown directly on DSO as for those grown with a SRO layer. Therefore, the lower intensity of the satellites observed for the latter, specially around the out-of-plane reflections [Fig. 2(d)], seems to indicate not a smaller out-of-plane polarization but rather a lack of modulation in the out-of-plane component of the polarization. This agrees with previous observations pointing out that a lower electrode helps charge neutralization, thereby preventing the formation of *c*-axis antiparallel stripes [33].

In general our results agree with theoretical calculations that predict the rotation of the polarization, from perpendicular to parallel to the film, under tensile strain. However, there is discrepancy between the phases we proposed and those predicted for PbTiO₃ films. An *aa* phase ($P_x = P_y$, $P_z = 0$) has been theoretically predicted for the present strain state [7–9,11], but it is incompatible with the observed *c*-axis polarization. Combinations of *aa* phase and *c* phase [8] or *aa* phase and *r* phase [34] have also been proposed, but they would imply two different out-of-plane lattice parameters, not observed here. The *r* phase proposed by us has been predicted by Landau models for PbTiO₃ under different (smaller) strain states [7], and by *ab initio* calculations for PTO under hydrostatic pressure [35]. The *ac* state has never been predicted for PTO. This discrepancy is in a sense not surprising, since most current theoretical calculations do not include electrical boundary conditions and are therefore not valid for very thin films. These boundary conditions have already been shown to affect the phase diagram of BaTiO₃ [36] and the domain structure of PbZr_{1-x}Ti_xO₃ under compressive strain [12].

In sum, fully coherent, very thin films of PbTiO₃ under tensile strain display a modulation in reciprocal space indicating stripe domains with the polarization rotated away from the tetragonal axis. This new low-symmetry state may provide a route towards achieving large piezoelectric coefficients in undoped PTO [35].

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Note added in proof.—Several months after the measurements presented here the satellites have disappeared. This provides further confirmation that their origin is polar and not structural. The reason for this charge neutralization may be related to the lower temperatures (around 273 K) accidentally endured by the samples during transport. According to Ref. [21], a monodomain state is expected at low temperatures.

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